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The Zone-Refining of a Lead-Bismuth Alloy

Edward James Westerman

THE ZONE-REFINING OF A LEAD-BISMUTH ALLOY

A Thesis

Presented to

the Faculty of the Department of Metallurgy

Montana School of Mines

In Partial Fulfillment

of the Requirements for the Degree

Bachelor of Science in Metallurgical Engineering

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CHAPTER I

THE PROBLEM

Zone-refining, the purification of a metallic ingot resulting from the passing over its length of a comparatively short molten zone, has been found useful in the purification of several metallic elements. The impurities present in an elemental metal are often more soluble in the molten zone than in the solid material, and are carried to one end of the bar in the molten zone. This molten-zone movement can be repeated any number of times on a metallic ingot, with the zone always being moved in the same direction. The process can be made more rapid by the simultaneous movement of several distinct molten zones over the ingot; these simultaneous zones may be melted in the ingot by several induction coils placed a short distance apart and surrounding the ingot, as in Figure 1. Until a low limiting concentration of impurity is reached in the ingot, each molten zone will carry more of the impurity to the end of the bar which is the last to solidify; this end of the bar may be cut off, leaving an ingot of high purity. Figure 2 shows the results of this refining procedure under certain specified conditions.

The purpose of this study was to determine if small amounts of bismuth impurity could be removed from lead by

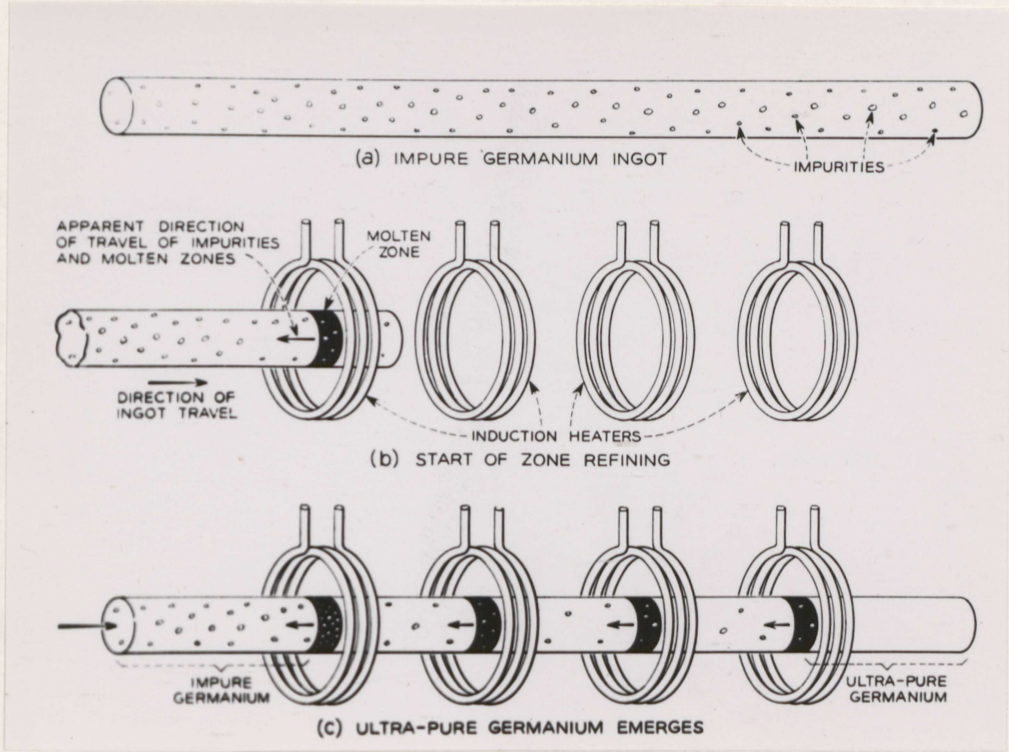

FIGURE 1

ZONE-REFINING TECHNIQUE
(FROM PFANN AND OLSEN, ZONE-MELTING)

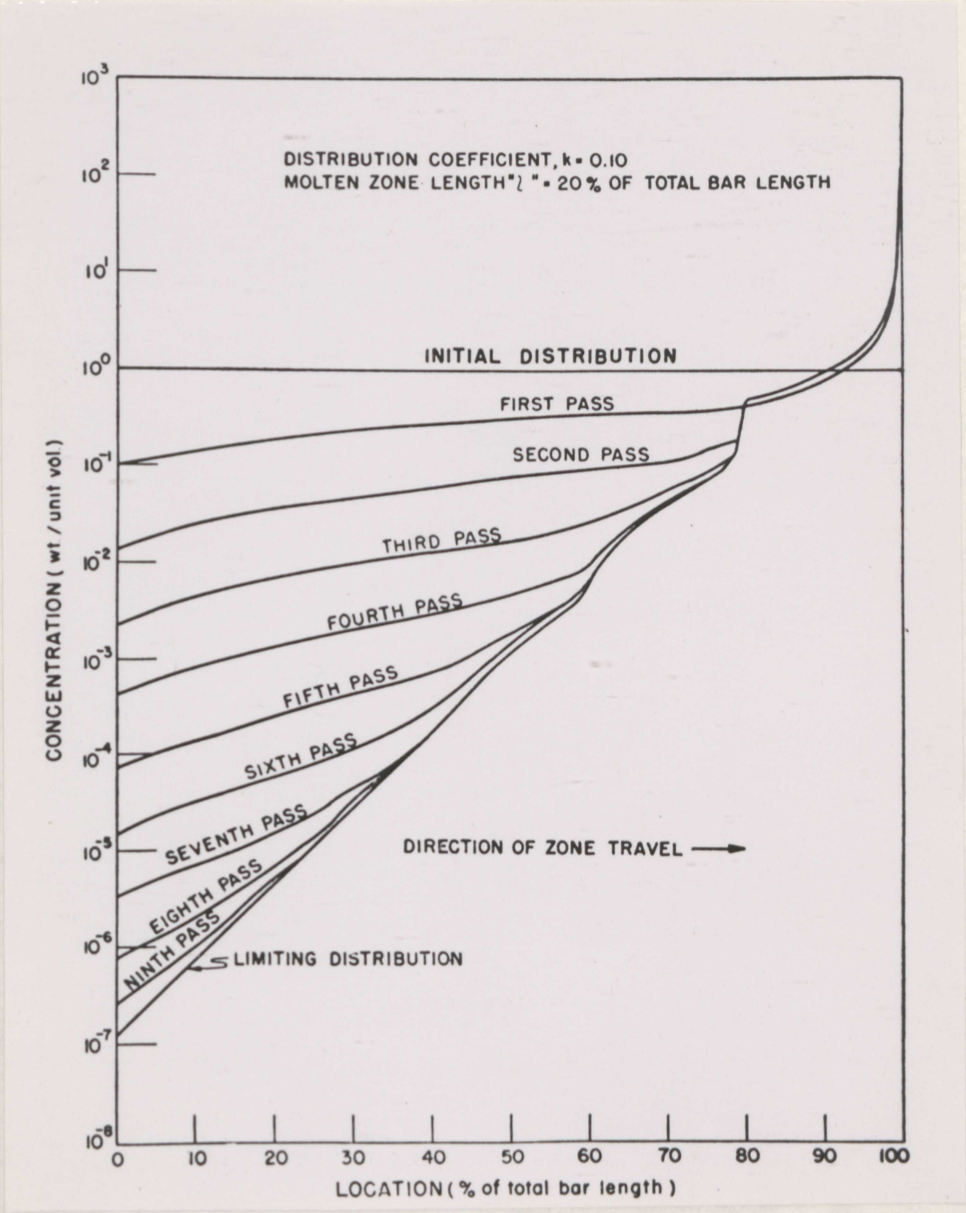

FIGURE 2

CONCENTRATION PROFILES IN A ZONE MELTED ROD (FROM BURRIS, CONTRIBUTION TO MATHEMATICS OF ZONE MELTING)

a zone-refining technique, and if the results obtained could be correlated with some of the theoretical mathematics developed to describe the zone-refining of a metallic ingot.

Because of the chemical similarity of lead and bismuth, it is difficult to commercially produce lead containing less than 0.001 per cent bismuth. Although some applications of lead favor a higher bismuth content, ultra-pure lead would also have many uses. The zone-refining techniques can surely be developed to yield this ultra-pure lead on a laboratory scale, and perhaps someday on an economically competitive commercial scale.

CHAPTER II

REVIEW OF THE LITERATURE

Zone-refining is a comparatively new metallurgical process, having been first reported in the literature in 1952.[1] Although the actual behavior during zone-refining of comparatively few binary systems has actually been investigated, the theoretical mathematics have been worked out in detail by several investigators.

I. APPLICATIONS

Zone-refining was first developed by W. G. Pfann of the Bell Telephone Laboratories, and was used to produce transistor germanium of extremely high purity.[2,3] At present, this purification of germanium is the major commercial application of zone-refining; although the refining is done on a small, laboratory scale, transistors are at present almost totally dependent on this zone-refining procedure. The germanium produced is probably the purest known manufactured material; the concentration of impurities throughout most of the ingot is less than

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[1]W. G. Pfann, "Principles of Zone Melting," Journal of Metals, IV(July, 1952), 750.

[2]Ibid.

[3]W. G. Pfann and K. M. Olsen, "Zone-Melting," Bell Laboratories Record, XXXIII(June, 1955), 202.

1 part in 10,000,000,000 parts of germanium.[4] The germanium ingot is converted from a polycrystalline material to a single crystal during the zone-refining procedure if a single crystal is placed at the leading end of the ingot. Pfann and Olsen report a molten-zone technique used to intentionally decrease the resistivity of transistor germanium by the controlled addition of a small amount of impurity, such as antimony. About 1 atom of additive per 100,000,000 atoms of germanium is required. A small pill of addition alloy is placed in a groove at the leading end of the ingot to provide the desired level of electrical conductivity. As a molten zone is started and moved down the ingot, there freezes out behind it a solid whose antimony concentration is always proportional to that in the zone. As little antimony is lost from the zone, the antimony concentrations in the zone and in the solid freezing from it remain essentially constant.[5]

Detwiler and Fox have successfully removed lead impurity from gallium by a zone-refining process.[6] Because of the low melting point and high thermal conductivity of gallium, the investigators were forced to put cooling coils between the

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[4] Ibid., p. 203

[5] Ibid.

[6] D. P. Detwiler and W. M. Fox, "Purification of Gallium by Zone-Refining," Journal of Metals Transactions, VII (January, 1955), 205.

heating coils in order to maintain several separate molten zones in the ingot.

Scientists at the Westinghouse Research Laboratories are purifying titanium by a "cage" process, in which the metal acts as its own crucible.[7] As titanium is very reactive and will combine with most container materials at high temperatures, the use of the "cage" process eliminates the possibility of a great deal of contamination from this source.

A titanium bar of square cross-section stands upright on a metal platform. It is surrounded by a large glass dome containing an atmosphere of argon or helium gas at low pressure. The molten zone produced in the bar by an induction coil does not melt the corners of the bar, for they rapidly lose heat to the surrounding atmosphere. The corners therefore remain rigid, and act as a "cage" in which the molten titanium is imprisoned. The platform is raised, causing the molten zone to move downward through the bar. Iron has been removed from titanium by this method, as it is more soluble in the molten titanium than in the solid, and is carried down to the bottom of the bar.

Tanenbaum, Goss, and Pfann have purified antimony and tin using a reciprocating method of passing molten zones

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[7]"Zone-Refining of Titanium," Light Metal Age, XIII (August, 1955), 19.

through a straight ingot.[8] The length of the stroke is equal to the distance d between the individual heaters used on the ingot. A stroke begins with the leading edge of the ingot about to emerge from the first heater. The ingot is advanced slowly, with respect to the heaters, a distance d, whereupon it is rapidly transferred to its starting position, transferring each molten zone to the next heater. These investigators maintain that this method effects a considerable economy of time and apparatus.

Pfann has further developed the theory of zone-refining with his concept of temperature-gradient zone melting.[9] In this technique a zone is made to move by impressing a temperature gradient across it. For example, a thin layer of molten aluminum-silicon alloy, sandwiched between two silicon slabs having a temperature gradient normal to the layer, will travel through the hotter slab. More silicon dissolves at the hotter interface than at the cooler one; this sets up a concentration gradient of silicon across the layer. The silicon gradually diffuses to the cooler interface and freezes, allowing the thin molten layer to move through the hotter slab of silicon. Temperature-gradient zone melting

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[8]M. Tanenbaum, A. J. Goss, and W. G. Pfann, "Purification of Antimony and Tin by a New Method of Zone-Refining," Metals Transactions AIME, CC(May, 1954), 762.

[9]W. G. Pfann, "Temperature Gradient Zone Melting," Journal of Metals Transactions, VII(September, 1955), 961-4.

can be adapted to zone-refining, the manufacture of complex transistors, the growing of single crystals, the joining of blocks of material, and other miscellaneous fabrication techniques.

Although most zone-refining processes to date have been laboratory-scale batch processes, Pfann has visualized the application of continuous zone-refining, which may make large-scale commercial operations possible.[10] This continuous process would make it possible to put a steady stream of impure germanium into the apparatus, and produce two streams of products: one of very pure germanium, and another of germanium carrying a large quantity of impurities. This impure stream could be refined again in a similar continuous process.

The recent developments in zone-refining show that it is no longer a laboratory curiosity. It is extremely versatile, and is constantly being developed to a point where it will be of tremendous value to the fields of physical and process metallurgy.

II. MATHEMATICS OF ZONE-REFINING

Although the theoretical mathematics of various phases of zone-refining have been worked out in detail by several investigators, this paper will be concerned only with the

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[10] W. G. Pfann, "Continuous Multistage Separation by Zone Melting," Journal of Metals Transactions, VII (February, 1955), 297-303.

more practical applications.

Pfann, after postulating certain conditions to be present, has developed a relationship describing the segregation during the normal freezing of an ingot, as well as for the single pass of a molten zone in zone-refining.[11,12] He has also related the ultimate distribution of impurity after infinitely many zone passes to k, the distribution coefficient, which is defined as the ratio of the concentration of the impurity in the solid phase to that in the liquid phase at equilibrium.[13] The conditions he postulates are these: (1) Diffusion in the solid is negligible. (2) Diffusion in the liquid is complete; that is, the concentration of impurity in the liquid is uniform. (3) The distribution coefficient, k, is a constant. Although these conditions are not met in practice, they provide a foundation on which to build a mathematical analysis.

Lord has derived a complex relationship for the determination of the impurity concentration at any point of an ingot after any number of zone passes.[14] His relationship

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[11]W. G. Pfann, "Principles of Zone Melting," Journal of Metals, IV(July, 1952), 747.

[12]Ibid., p. 748

[13]Ibid., p. 751

[14]Norman W. Lord, "Analysis of Molten-Zone Refining," Metals Transactions AIME, CXCVII(November, 1953), 1533.

has been somewhat simplified by Milliken, but is still formidable with respect to computational labor.[15] Generalized curves showing solute concentrations over length of ingot for various conditions of zone length, distribution coefficient, and number of passes seem to be the most practical contribution of the theoretical mathematics to zone-refining. Several of these curves have been worked out by Reiss,[16] and by Burris, Stockman and Dillon.[17]

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[15]K. S. Milliken, "Simplification of a Molten-Zone Refining Formula," Journal of Metals Transactions, VII(July, 1955), 838.

[16]Howard Reiss, "Mathematical Methods for Zone-Melting Processes," Metals Transactions AIME, CC(September, 1954), 1053-9.

[17]L. Burris, "Contribution to Mathematics of Zone-Melting," Journal of Metals Transactions, VII(September, 1955), 1017-23.

CHAPTER III

ZONE-REFINING THEORY

The fundamental theory behind zone-refining is quite simple and straightforward, and can be explained in terms of a binary equilibrium diagram.

I. THE LEAD-BISMUTH SYSTEM

As this investigation deals with the elimination of bismuth impurity from lead by zone-refining, the theory will be explained with reference to the lead side of the lead-bismuth equilibrium phase diagram.

It can be seen from Figure 3, the equilibrium diagram of the lead-bismuth system, that an addition of bismuth to pure lead lowers the liquidus temperature of the resulting solid solution. Only the lead side of the lead-bismuth system is shown in Figure 4, page 14. If a liquid of solute concentration C_o were cooled under conditions approaching equilibrium, the first solid particles of alpha phase to precipitate, of concentration kC_o, would be of lower bismuth content than the liquid with which they were in equilibrium. The distribution coefficient, k, is approximately 0.7 for this lead-bismuth alloy. For all points, down to the temperature where the last trace of liquid freezes to form a solid solution, the liquid phase constantly carries a

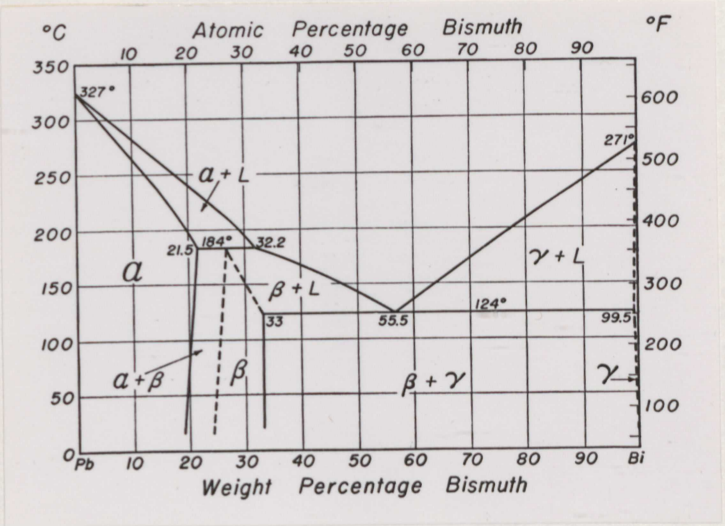

FIGURE 3

THE LEAD-BISMUTH SYSTEM
(FROM THE METALS HANDBOOK, 1948)

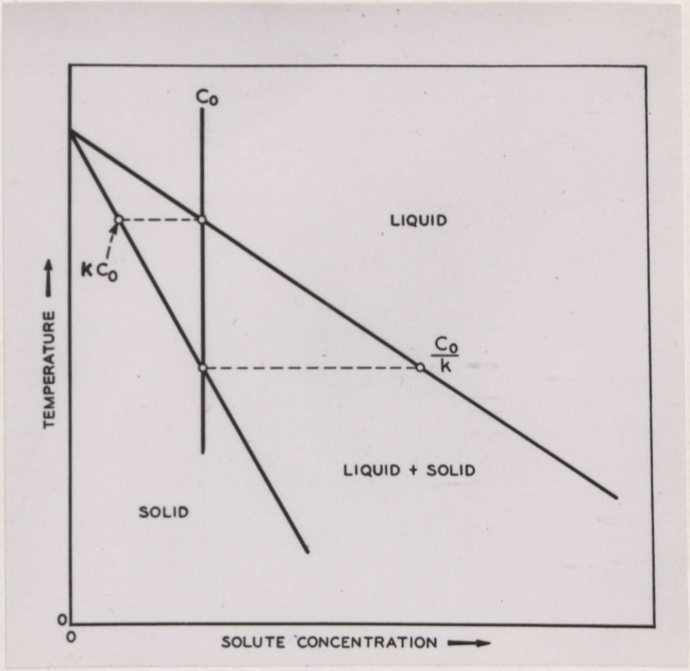

FIGURE 4

A SCHEMATIC VIEW OF THE LEAD SIDE OF THE LEAD-BISMUTH SYSTEM (FROM PFANN, PRINCIPLES OF ZONE-MELTING)

higher bismuth concentration than does the solid. This supplies the clue to the zone-refining phenomena. The leading end of the ingot, that is, the first end melted, solidifies to a composition carrying less bismuth than C_o. The molten zone, carrying a higher bismuth concentration, is moved away; overall equilibrium is not reached, and the first part of the bar to freeze will have a lower bismuth concentration than will the rest of the bar, with the last part of the bar to freeze containing the highest bismuth concentration. This phenomenon is identical to the "coring" or segregation that occurs in a molten ingot during solidification. As the zone is advanced down the bar, the liquid will be enriched, although at a decreasing rate, until it attains concentration C_o/k.[18] When this condition is attained the concentrations of solids entering and leaving the zone are the same, and hence no further change of concentration occurs in the zone or in the solid freezing from it until the end of the ingot is reached. At this time the zone diminishes in size, with the last portion freezing containing the highest bismuth concentration. This refining process is repeated as each molten zone is moved over the length of the bar.

If k, the distribution coefficient, is less than one, (as it is for the lead-bismuth example), additional impurity

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[18]W. G. Pfann, "Principles of Zone Melting," Journal of Metals Transactions, IV(July, 1952), 747.

will lower the liquidus temperature; under these conditions, the impurity will move in the same direction as the molten zone. If k is greater than one, the impurity will move in a direction opposite to the motion of the molten zone. This latter condition results in a comparatively inefficient zone-refining procedure, and one which will require more passes to give a comparative degree of purity.

II. THE ULTIMATE DISTRIBUTION

After repeated passes in one direction, an impurity distribution will be reached which cannot be changed by more passes. The effect may be likened to piling a given amount of sand against a vertical wall--there will be a maximum attainable height. This impurity concentration is called an ultimate or limiting distribution.[19] It has been proved that, as k grows smaller, the zone-refining procedure becomes more effective for any given set of conditions (and for k less than unity). If k were unity, no refining would take place, for the solid would be of the same composition as the liquid from which it solidified. For the lead-bismuth example k = 0.7, as determined from the equilibrium diagram; the nearness of this value to unity suggests that a zone-refining process will not be too efficient for this system, and that the

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[19] Ibid., p. 748

ultimate distribution of impurity will not attain the low concentration values possible with many other systems. Figure 5 shows the ultimate solute distribution for various values of k, as determined by theoretical mathematics.

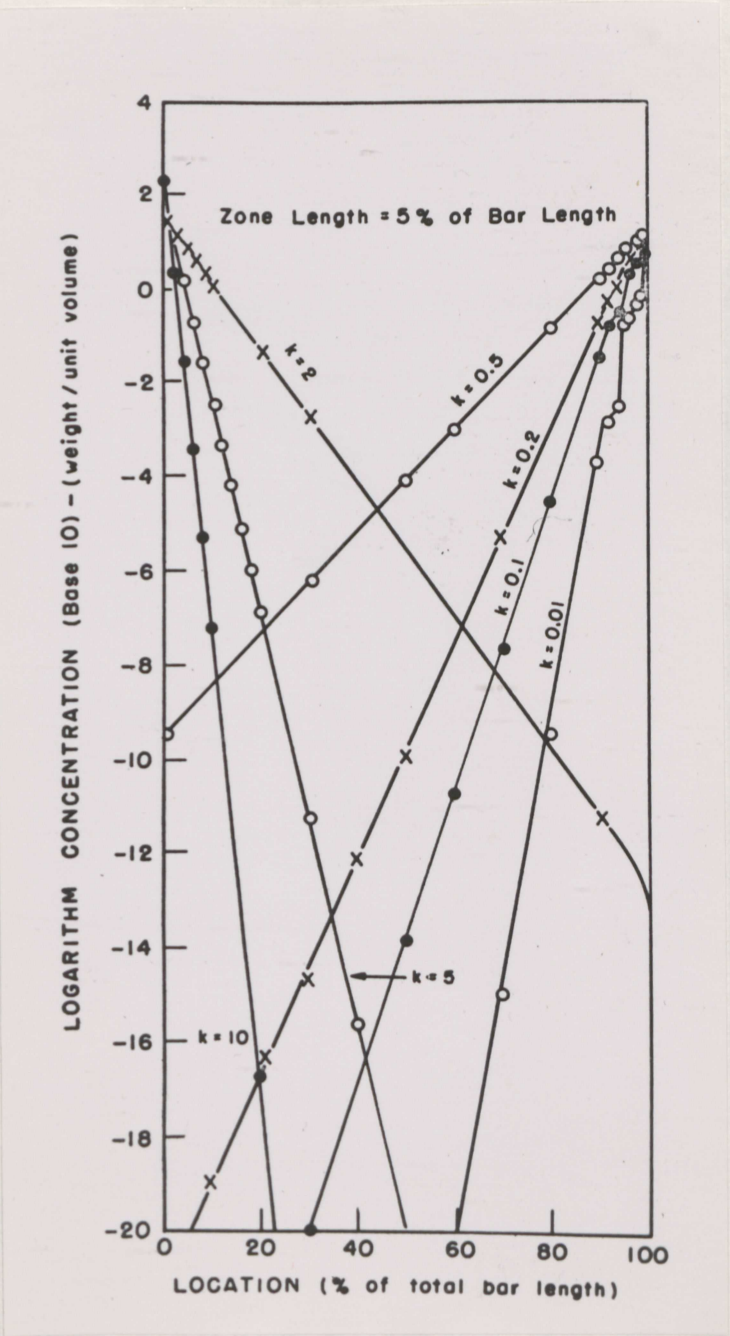

FIGURE 5

THE EFFECT OF k ON LIMITING DISTRIBUTION PROFILE
(FROM BURRIS, CONTRIBUTION TO MATHEMATICS OF ZONE MELTING)

CHAPTER IV

MATERIALS AND METHODS

An ingot of bismuth-contaminated lead, contained in a boat of fired refractory material, was slowly drawn through a high-frequency induction coil. The molten zone induced in the ingot by the coil was intended to carry the bismuth to the end of the bar which solidified last. After the zone-refining procedure had been carried out a certain number of times, the lead bar was cut into segments, dissolved in acid, and analyzed for bismuth content with the polarograph.

I. APPARATUS

Induction Furnace

An Ajax Electrothermic Company 3-kva high-frequency induction furnace supplied power to the induction coil. This furnace, of the spark-gap type, requires about 30 amps on a 240-v line to develop maximum power. The condenser and spark gap are water-cooled, and require a flow of 2 qts per minute for adequate protection against heat. The furnace, shown in Figure 6 with the complete zone-refining apparatus, has a spark-gap adjustment for roughly varying the power supplied to the coil.

The coil used during the entire course of the investigation is shown in Figure 7 on page 21; it is not a

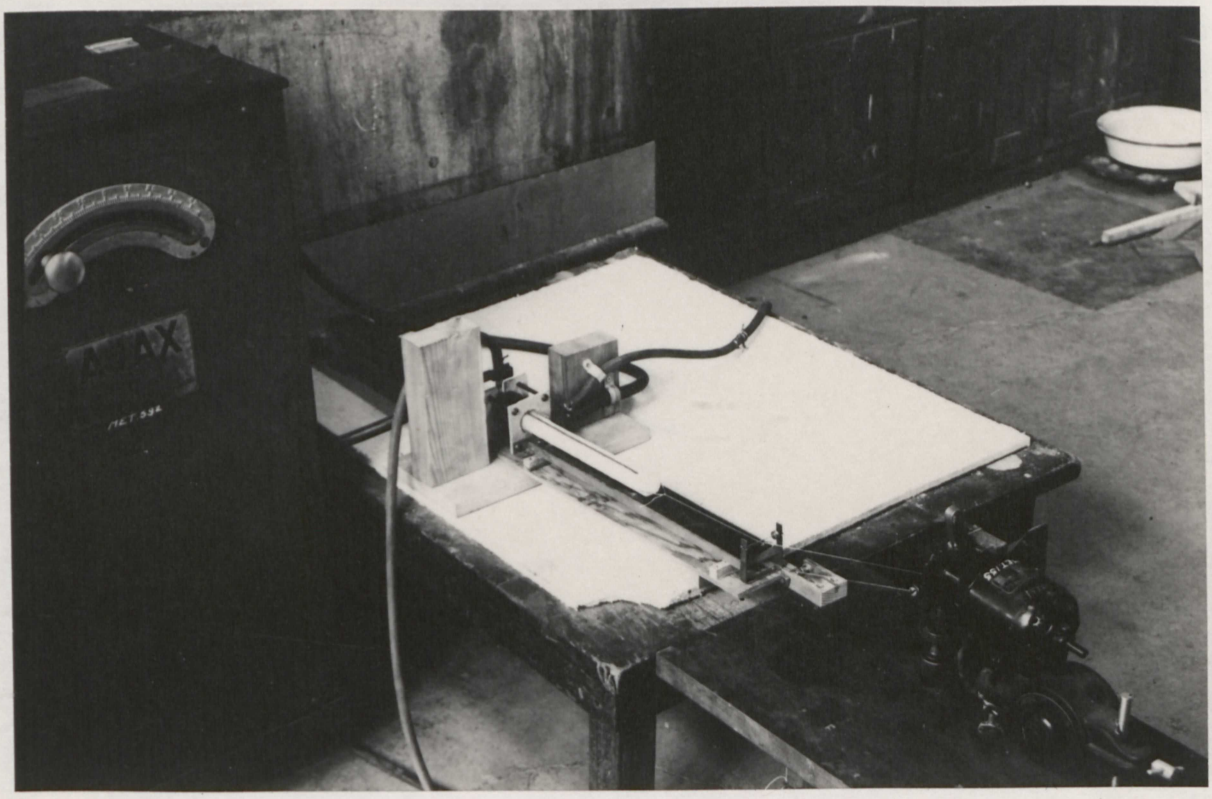

FIGURE 6

THE ZONE-REFINING APPARATUS

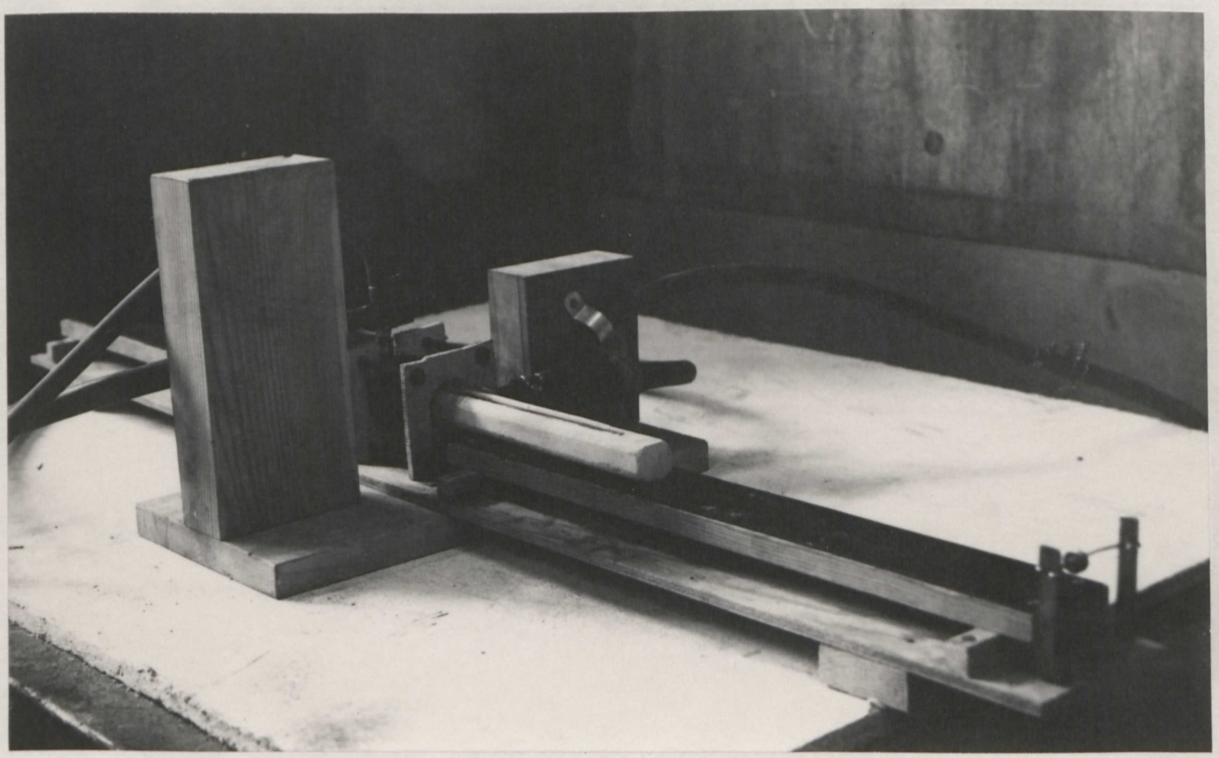

FIGURE 7

INDUCTION COIL AND BOAT

commercial coil, but was hand-made by a former student. It is open on both ends, and has an inside diameter of 1 1/4 in. It is made of 20 turns of partially flattened 3/16-in. outside diameter copper tubing and is 2 in. in length. Cooling water is forced through the coil during its use.

Boat-drawing Apparatus

The boat-drawing apparatus, shown in Figure 8, is a small winch powered by a variable-speed a-c motor through a speed-reducing gear train. The gears used in this apparatus were taken from a large clock; the motor is a small all-purpose unit containing a built-in variable rheostat. The winch is a small brad, turning at a speed which may be varied between 1 and 9 revolutions per minute, over which the cotton boat-drawing thread is looped once. The end of the thread which is not attached to the boat is held taut by a 250-g counterweight. As the brad slowly turns, the counterweight drops, and the boat is drawn through the induction coil. A variable rheostat was connected in series with the motor to effect a further reduction in speed.

Polarograph

The polarograph used for the quantitative bismuth analysis is a Sargent-Heyrovsky' Model XII recording-type instrument. A thermostatically controlled water bath

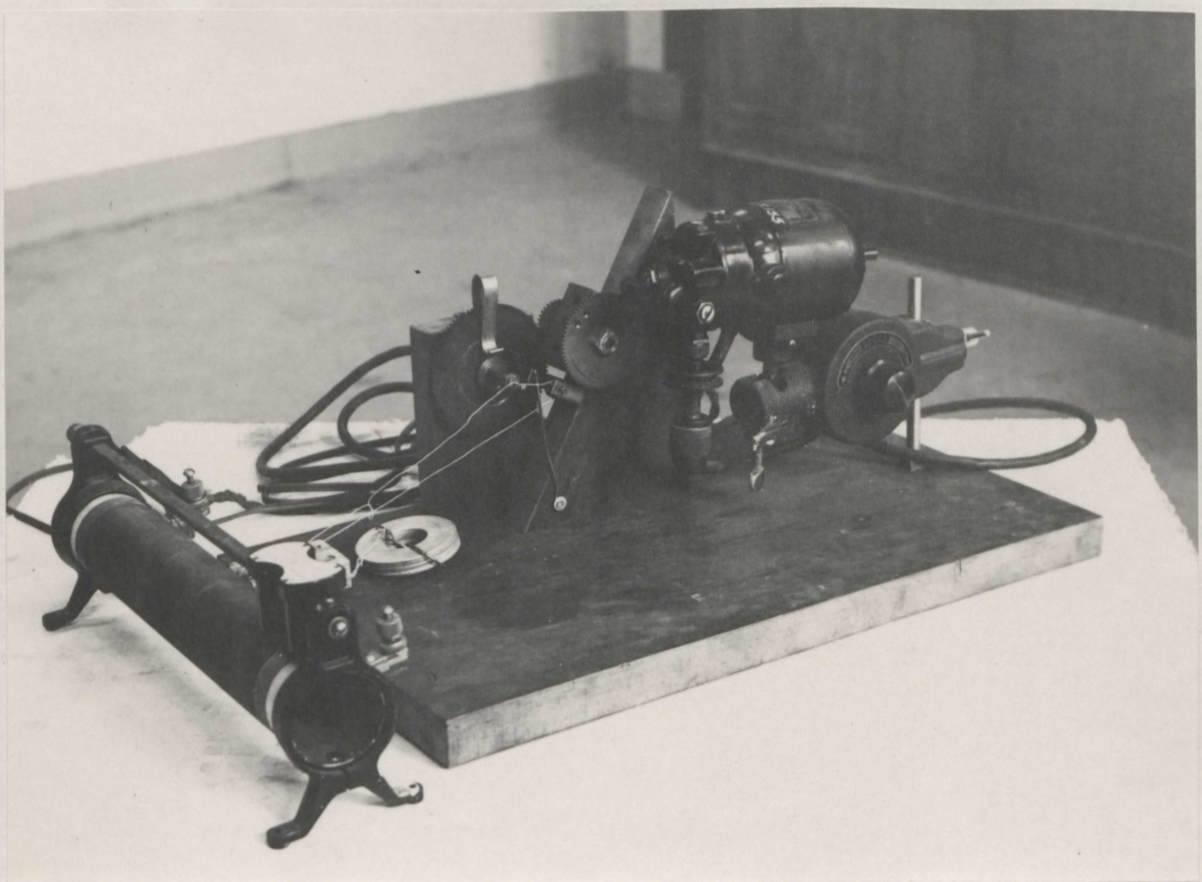

FIGURE 8

THE BOAT-DRAWING APPARATUS

(set at 24.7 C) and 10-ml electrolysis vessel were used in conjunction with the polarograph, as shown in Figure 9.

II. MATERIALS

Lead

Pueblo Brand Test Lead, C. P., containing approximately 0.001 per cent bismuth, was used to make up the bismuth-lead alloys for the zone-refined ingots. This lead is produced by the American Smelting and Refining Company at their Globe Plant in Denver.

Bismuth

Baker and Adamson lump bismuth metal, 99.8 per cent pure, was added to the test lead to make alloys of the desired composition.

Boat Material

A highly refractory material containing approximately 20 per cent kaolin, 40 per cent silica sand, and 40 per cent milled fire clay was used to make the boats containing the alloy. Although this material did not fire hard at cone 16 (2650 F), the boats were quite durable after a heating for one hour at 2000 F followed by furnace cooling. They were used in this semi-fired condition without any loss due to breakage, for extreme care was used in handling them at all times.

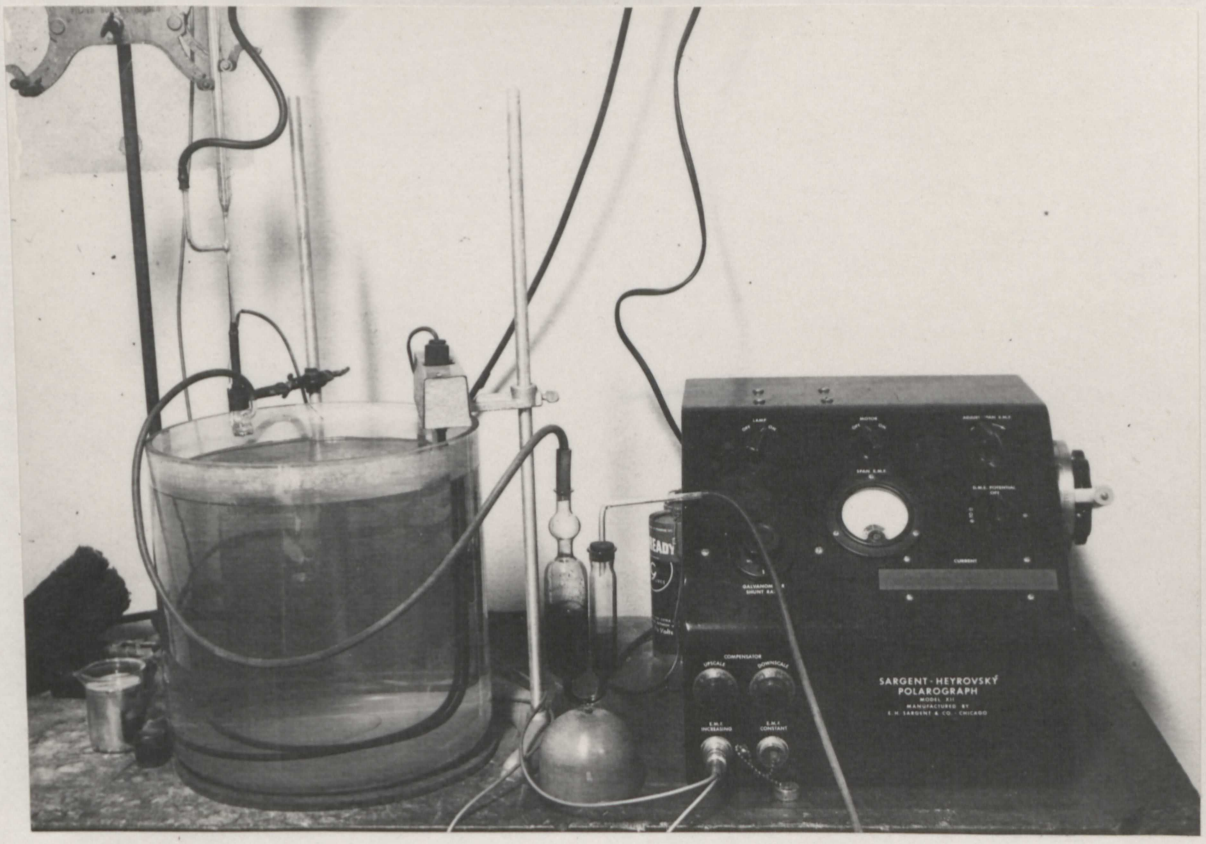

FIGURE 9

THE POLAROGRAPHIC APPARATUS

A wooden mold with removable sides was used to form the boats from the damp, stiff refractory mixture. The mold, a fired boat, and an alloy-filled boat are shown in Figure 10. As the rectangular boats formed in this manner were slightly too large to pass through the induction coil, the edges of the boats were rounded off with a spatula after air-drying and before firing.

The boats were 14 in. in length, 7/8 in. wide, and 7/8 in. high after firing. The lead groove measured 12 in. long by 1/4 in. wide by 5/16 in. deep.

III. PRELIMINARY WORK

Lead Ingots

About 150 g. of lead alloy was needed to fill the lead groove in each boat. An alloy of approximately 0.001 per cent bismuth, that is, test lead, was used to fill several boats. The next set of three boats were filled with lead containing approximately 0.05 per cent bismuth.

The desired alloy was melted in one batch in a silica crucible, and stirred with a carbon rod to insure homogeneity. The boats to be filled were preheated to 600 F to prevent the premature solidification of lead during the pouring operation, and to minimize "coring" during non-equilibrium freezing of the ingot. The ingots were allowed to furnace-cool.

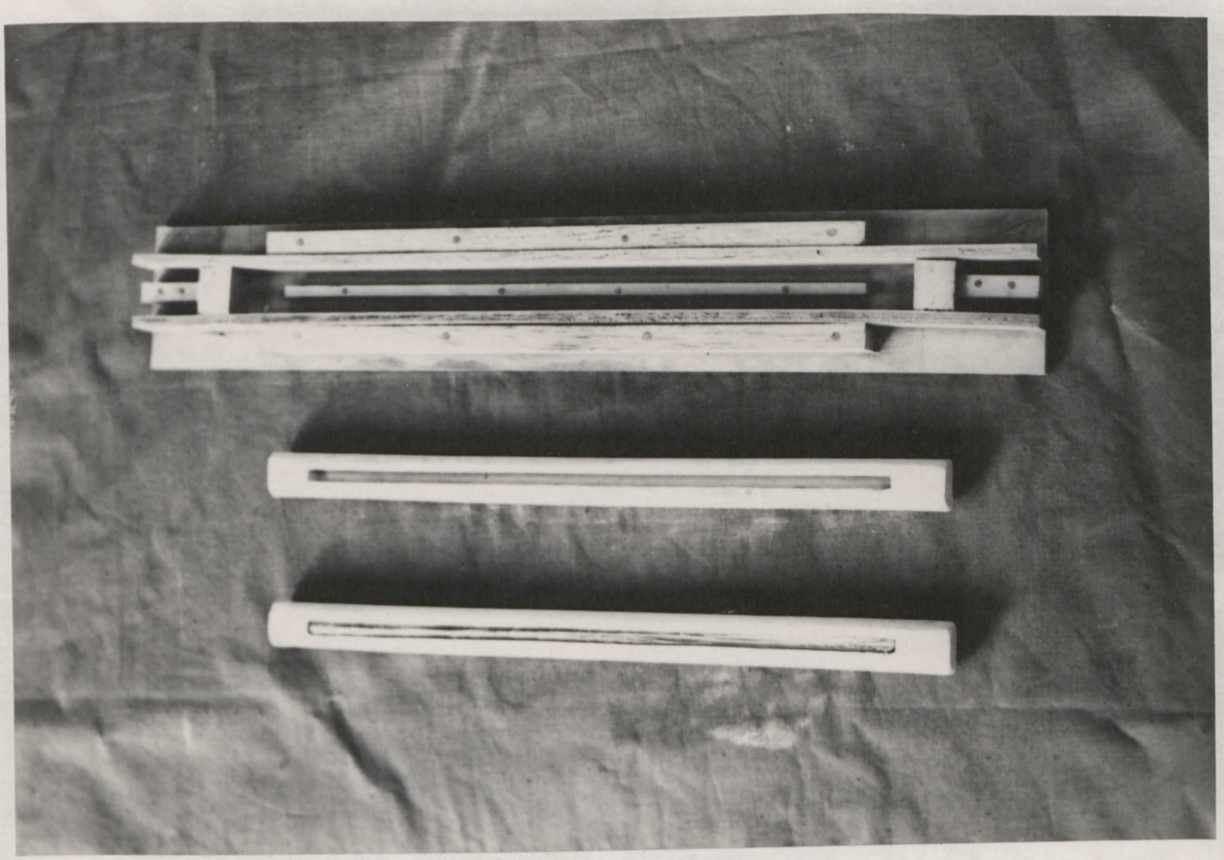

FIGURE 10

BOAT-MOLD, FIRED BOAT, AND ALLOY-FILLED BOAT

Standardization of the Polarograph

The polarograph-standardization procedure followed as closely as possible the analytical procedure recommended by Kolthoff and Lingane for the determination of bismuth in lead.[20] The required amount of bismuth was added as a standard bismuth nitrate solution to a small sample vial; then 1.5 ml of 4 N H_2SO_4, 3 ml of 1 M sodium citrate, and 1 drop of methyl red was added. The solution was neutralized with concentrated NH_4OH until the methyl red turned a salmon color, at a pH of about 5.5, then made up to a volume of 10 ml with distilled water. The methyl red acted both as an indicator and as a current maximum suppressor.

The solutions were all purged with gaseous nitrogen for 5 min immediately prior to the polarographic procedure; this removed dissolved oxygen from the solutions. A drop time of 4 seconds and a span emf of 2 v were used during polarography. It was found that the half-wave potential for the reduction of bismuth was about 0.41 volts when the samples were prepared in this manner.

IV. EXPERIMENTAL PROCEDURE

Zone-refining

The refractory boat, containing the lead ingot, was placed at the start of each pass so that it was just about

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[20] I. M. Kolthoff and J. J. Lingane, Polarography, Volume 2 (New York:Interscience Publishers, 1952), p. 606.

to emerge from the induction coil. It remained stationary in this position for about 5 min, while the induction coil melted a molten zone in the leading end of the ingot. After a molten zone had been produced, the boat-drawing apparatus was started; the ingot was then drawn through the coil. A rate of 1 cm per min was used on all passes during the course of the experimentation.

The molten zone was kept as short as possible by a constant regulation of power to the induction coil, but it was found that a zone of 3-in. length was the shortest that could be steadily maintained with the apparatus. This 3-in. zone length was maintained whenever possible.

The molten zone was passed 3 times over an ingot of test lead, and 5 times over a lead ingot containing about 0.05 per cent bismuth. After the zone-refining operation, the test-lead ingot was cut into 1-in. samples and analyzed, whereas the 0.05 per cent bismuth ingot was cut into 1/2-in. samples for analysis. As the latter ingot gave the more significant results, the polarographic analysis procedure will be explained in terms of it, although the procedures used for both are essentially the same.

The ingot was cut into 1/2-in. lengths, weighing approximately 7 grams apiece. Certain of these segments were chosen as representing critical concentration areas on the bar; these were analyzed, while the rest were set aside. Samples of the

0.05 per cent bismuth alloy which had been taken while the ingots were being poured and which were not zone-refined were also analyzed.

Polarography

The polarographic method used was adapted from that suggested by Kolthoff and Lingane for the determination of impurities in lead.[21]

The lead samples were dissolved in 50 ml of 1:4 HNO_3. The solutions were transferred to 100 ml volumetric flasks, treated with 5 ml of H_2SO_4 to precipitate the lead as lead sulfate, then made up to volume. Aliquots of 50 ml were taken from the flasks, and evaporated to fumes of SO_3 on a hot plate. Concentrated NH_4OH was added in slight excess to precipitate the bismuth as a hydroxide, and the solutions were left to digest on a hot plate for a short length of time. Each solution, with its residue, was transferred to a centrifuge tube and centrifuged. The precipitates, containing bismuth, iron, and a little lead, were saved, while the solutions were decanted off and discarded. Each precipitate was dissolved in 1.5 ml of 4 N H_2SO_4, and 3 ml of 1 M sodium citrate was added. One drop of methyl red was added to each sample as a maximum suppressor and indicator; each solution was then neutralized to a pH of 5.5 with

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[21] Ibid.

concentrated NH_4OH, made up to 10 ml volume with distilled water, and placed in an electrolysis cell. Dissolved oxygen was purged from the solutions by a 5-min bubbling with gaseous nitrogen immediately prior to the polarographic procedure. During polarography, an atmosphere of nitrogen was maintained over the surface of the solution being analyzed.

A span emf of 2 v was used on the polarograph, although each run was made between 0 and 1 v. The polarograms were recorded on Kodak Royal Bromide F-1 paper, developed in Dektol for about 14 sec, and fixed for 10 min in an F-5 fixing solution.

CHAPTER V

RESULTS AND DISCUSSION

The bismuth gradient in the ingot, resulting from the zone-refining procedure, did not compare closely with that predicted by theory. The process could be improved in several ways to produce more efficient refining.

I. POLAROGRAPHIC RESULTS

The bismuth ion concentration proved to be quite easily determined by the polarographic apparatus employed, providing that the bismuth was in the pure form (as a standard) or in fairly high concentration (in the 0.05 per cent bismuth alloy). The bismuth content of the test-lead ingot could not be determined by polarographic means because of the presence of a small interfering wave which occurred at a potential slightly below the reduction potential of bismuth. On the assumption that the interfering wave was ferric iron, an attempt was made to eliminate it by reduction with a small amount of hydroxylamine hydrochloride; the attempt failed. It was at this time that an ingot was made containing 0.05 per cent bismuth, as it was reasoned that the small interfering wave would be suppressed by the high shunt ratio required for the polarography of this comparatively high bismuth concentration. The interfering wave did not appear

at all on these samples; the bismuth waves were well-formed and easily measured.

The quantitative method used to prepare the polarographic samples apparently has some faults, for a few results were obtained which were too low to be attributed to inhomogeneities in the ingot; they must be attributed to analytical procedure. At one stage in the preparation of the samples the bismuth was precipitated as a hydroxide and centrifuged, after which the fluid was removed from the precipitate by decantation. It was noted that, unless extreme caution was observed, a small portion of the flocculent precipitate could be lost at this time. This may explain the erratically low results of several of the analyses. Regulation of pH during the sample preparation is also critical; too low a pH during bismuth precipitation will cause a loss of bismuth by solution, whereas too high a pH in the polarographic solution will cause low results for bismuth due to precipitation.

II. BISMUTH GRADIENT

The concentration of bismuth at various points along the zone-refined 0.05 per cent bismuth bar after 5 passes is shown in Figure 11. Assuming $\underline{k}$ for bismuth in lead as 0.7, it was also possible to interpolate the graphical data given by Burris to determine the approximate theoretical bismuth

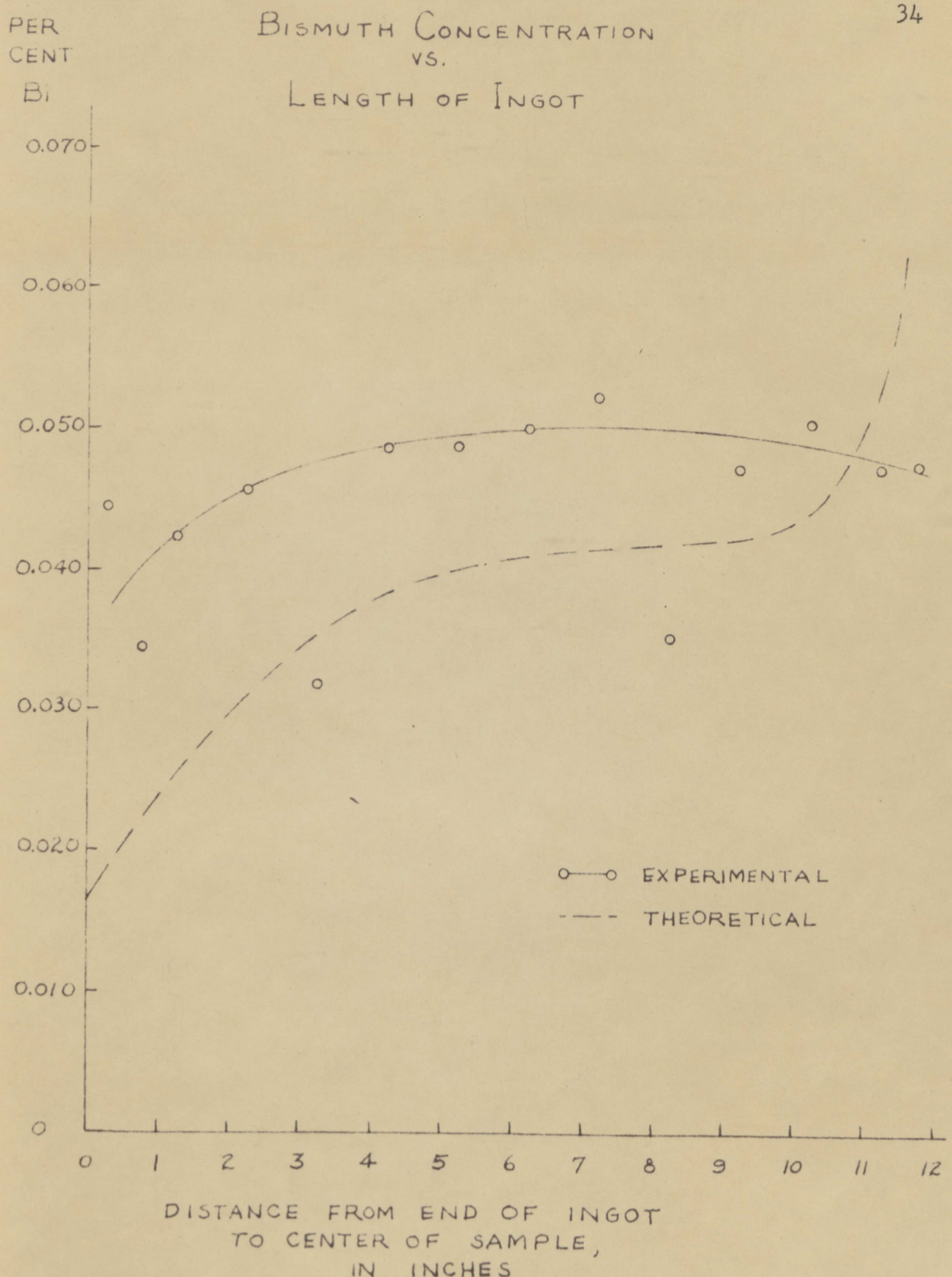

FIGURE 11. EXPERIMENTAL AND THEORETICAL BISMUTH GRADIENTS

gradient to be anticipated in the bar. This theoretical bismuth gradient is also plotted in Figure 11.[22]

Lord's exact equation cannot be applied to check the correlation of the experimentally determined bismuth gradient with mathematical theory, for it can only be used to find the solute concentration over a length x extending from $x = 0$ to $x = L - nl$, where L is the total length of the ingot, n is the number of passes, and l is the zone length.[23] As 5 passes were used in the experiment, and the zone length was equal to 1/4 l, it can be seen that the upper limit of x would be a meaningless negative number.

The experimentally determined gradient indicates that the zone-refining method used gave poorer refining results than could be theoretically anticipated. Although there appears to be some depletion of bismuth in the first 2 in. of ingot, there is not nearly the gradient described by the theoretical curve. The zone-refining process could be altered in several ways to achieve better refining:

1. The rate of movement of the lead ingot through the coil should be decreased, so that the solidification process might more nearly approach equilibrium conditions. The rate

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[22]Burris, op. cit., p. 1018

[23]Reiss, op. cit., p. 1059

of 1 cm per minute appears to be too rapid to allow ample time for segregation of the bismuth.

2. The boat-drawing apparatus should be improved. The motion of the boat through the coil is too irregular and jerky to allow quiet freezing at the solid-liquid interface.

3. Some provision should be made for a finer and more easily controlled source of power to the induction coil, so that the length of the molten zone could be regulated at any drawing speed desired.

4. The boats should be hard-fired or glazed for best results. Small pieces of sand kept falling from the semi-fired boats; these pieces of sand added to the friction of the boats on the drawing-platform, and contributed to the jerky motion.

CHAPTER VI

SUMMARY AND CONCLUSIONS

A lead ingot, 12 in. long and containing 0.05 per cent bismuth, was passed 5 times through an induction coil at the rate of 1 cm per min. The 3-in. molten zone induced at each pass was intended to carry the bismuth to the last end of the bar to solidify. Although a slight bismuth gradient was effected in the ingot, the refining was not as effective as prescribed by theory. The bar could be refined to some degree by many passes such as the 5 it had experienced, but better results could be obtained by improving the procedure and apparatus used.

The concentration of bismuth in the supporting solutions described can be very accurately determined by polarographic means; this was proved by a very good, linear standardization curve between 200 and 1000 micromolar bismuth. Errors may be introduced in the analysis of bismuth in lead, however, unless a great deal of care is taken in the preparation of the polarographic samples. This holds true, of course, for any quantitative analysis work.

CHAPTER VII

RECOMMENDATIONS FOR FURTHER STUDY

The lead-bismuth system should be zone-refined under various conditions of zone length, rate of boat movement, ingot length, and composition, so that the most efficient refining procedure may be determined. The results of experimentation should be compared with the theory whenever possible. The study should be extended systematically to other binary and ternary systems, so that a general outline of behavior could eventually be predicted for any set of conditions imposed.

Zone-refining is a new and versatile tool of the metallurgist; it has a great potential that has not been fully realized. Metallurgical research is needed to develop its many unique applications.

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APPENDIX A

POLAROGRAPH STANDARDIZATION

Sample Strength, Micromolarity in Bi	Shunt	Wave Height, in 60ths of an Inch	Product of Wave x Shunt
200	5	142	710
300	5	198	990
600	10	192	1920
800	10	255	2550
1000	20	156	3120

APPENDIX B

ANALYSIS OF LEAD-BISMUTH INGOT

Distance from Leading End of Ingot to Center of Sample	Sample Weight	Wave Height x Shunt	Micro-molarity	Per Cent Bismuth
1/4 in.	7.6732g	2580	816	0.0445
3/4	7.9440	2090	654	0.0344
1 1/4	7.8793	2520	794	0.0422
2 1/4	6.9270	2410	760	0.0459
3 1/4	6.5106	1610	495	0.0318
4 1/4	6.6299	2440	770	0.0486
5 1/4	6.6562	2460	774	0.0486
6 1/4	7.3175	2770	877	0.0501
7 1/4	6.8650	2710	858	0.0522
8 1/4	7.0775	1920	598	0.0353
9 1/4	6.8508	2460	775	0.0473
10 1/4	6.6157	2540	803	0.0507
11 1/4	6.4379	2320	728	0.0473
11 3/4	5.4932	2010	626	0.0476